Parametric Study of a Corrosion Model Applied to

Lead-Bismuth Flow Systems[*]

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Abstract:

The corrosion of steels exposed to flowing liquid metals is influenced by local and global conditions of the flow systems. Despite of this, most existing corrosion models only consider the average values based on local conditions. The present study refines a model for flowing liquid metal under non-isothermal conditions. The model is based on solving the mass transport equation in the boundary layer. Two kinds of flows are investigated: through an open pipe system and through a closed loop system. The model is applied to a Lead-Bismuth eutectic (LBE) test loop. A parametric study illustrates the effects of the global temperature profile on corrosion. The study provides important insight to the design, operation and testing of such loop systems.

Key words: liquid metal corrosion, corrosion model, turbulent flow.

1. Introduction

Corrosion of containment and structural materials presents a critical challenge in the use of liquid lead-bismuth eutectic (LBE) or lead as a nuclear coolant in Accelerator-Driven Systems and advanced reactors. Properly controlling the oxygen activity in LBE to mitigate corrosion proves effective under certain conditions. Liquid metal corrosion can proceed via dissolution at very low oxygen concentration, and through surface oxidation and reduction of surface oxides at higher oxygen concentrations. Corrosion rate is typically a function of local temperature and flow velocity. However, corrosion and precipitation rates and distributions can depend strongly on the global temperature distribution, limiting the applicability of many corrosion models.

The majority of corrosion research focuses on the influence of the local conditions, in particular the velocity of the liquid and the local temperature. The global temperature profile, or the global distribution of the boundary concentration of the corrosion product, is usually neglected in the analysis of corrosion kinetics. The corrosion rate q is calculated using the following equation [1]:

$$q = K(c_s - c_b),\tag{1}$$

where K is the mass transfer coefficient dependent on the flow velocity, c_s is the corrosion product concentration at the liquid-solid interface dependent on the local temperature, and c_b is the concentration in the bulk flow and is often set to $c_b \approx 0$ [1]. Based on the above equation, the corrosion rate is determined by the hydrodynamic parameters and the local temperature. However, many industrial flow systems subject to corrosion are under non-isothermal conditions, and the global temperature profile may have a profound effect on the rate of material corrosion. As a result, an accurate

description of the corrosion phenomena that take place in a non-isothermal system can be accomplished only if the global conditions are taken into consideration.

A kinetic model incorporating the global condition has been developed by He & Li [2]. The model demonstrates that the global temperature profiles have significant effects on corrosion and precipitation phenomena. However, this model is limited for simple loop flows, and there is a missing term in the solution of the boundary layer concentration.

The present study extends the kinetic model for loop flows to more general cases. We first derive a general kinetic solution by solving the governing concentration equation in the boundary layer. Two types of flows are examined: a closed loop flow and an open pipe flow. From the non-local analysis, we elucidate the difference of the corrosion phenomena between the closed loop flow and the open pipe flow. We also investigate the effects of global temperature profiles on the distribution of the corrosion and precipitation. This information will be very useful for the design and operation of liquid metal cooled systems.

2. Theory

2.1 Model and general solution

In general, the following equation is used to calculate the mass transport in flowing liquid system:

$$\frac{\partial c}{\partial t} + (\vec{u} \cdot \nabla)c = D\nabla^2 c + q , \tag{2}$$

where c is the concentration of the corrosion product under study, $\vec{u}$ is the velocity vector of the liquid, D is the mass diffusion coefficient, and q is the net production

(consumption) rate due to chemical reactions in the liquid. In the present study, we neglect the reaction of the corrosion product in the bulk of the liquid and set $q = 0$.

For a fully turbulent flow, it is reasonable to assume that the mixing flow homogenizes the bulk concentration and one only needs to solve the transport problem inside the boundary layer, where convection is dominant in the longitudinal direction (flow direction) and diffusion is dominant in the transverse direction. For the steady state case, the governing equation in the boundary layer can be written as

$$u \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial y^2} \ , \tag{3}$$

where x and y are coordinates in the axial and transverse directions, respectively.

For liquid metals, the diffusion coefficient is much smaller than the kinematic viscosity. The Schmidt number ($Sc = \upsilon / D$, where υ is the kinematic viscosity) is very large. The higher the value of Sc, the thinner the diffusion layer will be. For this case, the velocity boundary layer thickness is large compared to the species mass transfer boundary layer. It is conventional to approximate that the velocity is linear in the transverse coordinate y in the diffusion layer, that is

$$u = \gamma y \ , \tag{4}$$

where $\gamma = \lambda V^2 / 2\upsilon$, λ is the Fanning friction factor and V is the bulk flow velocity outside the boundary layer. Introducing

$$\xi = \frac{x}{L} \ , \ \eta = (\frac{\gamma}{DL})^{1/3} y \ ,$$

where L is the reference length in the main flow direction, the following dimensionless equation is obtained:

$$\eta \frac{\partial c}{\partial \xi} = \frac{\partial^2 c}{\partial \eta^2} \,. \tag{5}$$

The boundary condition is:

$$\text{At } \eta = 0 \,, \; c_w = c_w(\xi) \,, \tag{6}$$

and the concentration in the bulk flow is limited with an average value c_0^b. Now we expand the concentration in a Fourier series

$$c = \sum_k Y_k(\eta) \exp(2\pi i k \xi) \,. \tag{7}$$

We also expand the concentration at the wall into a Fourier series

$$c_w = \sum_k c_k \exp(2\pi i k \xi) \,, \tag{8}$$

Each Fourier harmonics, $Y_k(\eta)$, satisfies the following ODE:

$$2k\pi i \, \eta Y_k(\eta) = \frac{d^2 Y_k(\eta)}{d\eta^2} \,. \tag{9}$$

For $k = 0$, the solution of equation (9) is

$$Y_0(\eta) = \frac{(c_0^b - c_0)}{\delta_D} \left(\frac{DL}{\gamma}\right)^{1/3} \eta + c_0 \,, \tag{10}$$

where δ_D is the thickness of concentration boundary layer and c_0 is the average wall concentration..

For $k \neq 0$, the solution of equation (9) is

$$Y_k(\eta) = a_k Ai((2\pi k i)^{1/3} \eta) + b_k Bi((2\pi k i)^{1/3} \eta) \,, \tag{11}$$

Where Ai is the Airy function. Considering the boundary condition, we obtain

$$b_k = 0 \,, a_k = \frac{c_k}{Ai(0)} \,, (k \neq 0) \,.$$

Then the solution of Equation (3) is

$$c = \frac{(c_0^b - c_0)}{\delta_D} (\frac{DL}{\gamma})^{1/3} \eta + c_0 + \sum_{k \neq 0} a_k Ai((2\pi ki)^{1/3} \eta) e^{2\pi ki \xi} , \qquad (12)$$

The species flux at the wall into the liquid can be calculated by

$$q = -D \frac{\partial c}{\partial y}\Big|_{y=0} = (\frac{2\pi D^2 \gamma}{3L})^{1/3} \frac{1}{\Gamma(1/3)} \sum_{k \neq 0} a_k k^{1/3} \exp(2\pi ki \xi + i \frac{\pi}{6}) + \frac{D}{\delta_D}(c_0 - c_0^b), \quad (13)$$

where Γ is the Gamma function.

The $k = 0$ case is treated incorrectly in Ref. [2], leading to solutions without the typical mass transfer term that is only dependent on the average quantities, while the distribution dependent on global conditions remains the same.

2.2 Solution for open pipe flow

Let us first consider a fully developed turbulent flow in an open isothermal pipe with a constant species concentration at the wall, that is $c_w = c_0$ and accordingly $a_k = 0$. Based on equation (12), the solution of the concentration in the boundary layer is

$$c = \frac{(c_0^b - c_0)}{\delta_D} (\frac{DL}{\gamma})^{1/3} \eta + c_0 , \qquad (14)$$

The above equation indicates that for the open isothermal pipe flow, the concentration in the mass transfer boundary layer is linear in the transverse coordinate y. From this equation,

$$q = \frac{D}{\delta_D}(c_0 - c_0^b) = K(c_0 - c_b) , \qquad (15)$$

where $K = D / \delta_D$ is the mass transfer coefficient, c_b is the bulk concentration and $c_b \approx 0$ [1].

Eq. (15) has been used by many authors to estimate the corrosion rate in flowing liquid systems. According to the above analysis, this equation can only be used for the isothermal condition, or equivalently a constant concentration at the boundary. The boundary layer has to be fully developed. Thus the application of Equation (15) to isothermal sections in non-isothermal loops is limited.

For the non-isothermal cases, the corrosion rate should be calculated as

$$q = (\frac{2\pi D^2 \gamma}{3L})^{1/3} \frac{1}{\Gamma(1/3)} \sum_k a_k k^{1/3} \exp(2\pi ki\xi + i\frac{\pi}{6}) + K(c_0 - c_0^b). \qquad (16)$$

For these cases, the local corrosion rate is composed of two parts: the average part and the part due to the global concentration gradient along the wall.

2.2 Solution for closed loop flow

Because the liquid in a closed loop is not renewed, the total amount of corrosion should equal to the total amount of precipitation in the entire loop at the steady state

$$\int_0^L q dx = 0, \qquad (17)$$

where L is the loop length. Substituting equation (13) into equation (17), we find $c_0^b = c_0$. So the boundary layer concentration and the corrosion rate are:

$$c = c_0 + \sum_{k \neq 0} a_k Ai((2\pi ki)^{1/3}\eta)e^{2\pi ki\xi}, \qquad (18)$$

$$q = (\frac{2\pi D^2 \gamma}{3L})^{1/3} \frac{1}{\Gamma(1/3)} \sum_{k \neq 0} a_k k^{1/3} \exp(2\pi ki\xi + i\frac{\pi}{6}). \qquad (19)$$

For an isothermal closed loop, from equation (18), we find $c = c_0$, this means that there is no concentration gradient between the bulk flow and the boundary. So there is no corrosion in a closed isothermal loop at the steady state. For the non-isothermal closed

loop case, the mean corrosion rate is zero, while local corrosion rate depends on the global boundary concentration distribution.

3. Analysis results

The above model is applied to a Material Test loop (MTL) in our Laboratory. The MTL is a non-isothermal closed loop and is used to study the corrosion of various materials in flowing Lead-Bismuth eutectic (LBE). It uses a recuperator, a heater and a heat exchanger to set and control the temperature profile. LBE comes out of the pump at a low temperature, passes through the recuperator shell side and the heater, and reaches the highest temperature at the test section. On the return path, the temperature decreases through the recuperator tube side and the heat exchanger, and reaches the lowest temperature. The temperature profile is shown in Fig.1 [3].

In oxygen control LBE systems, we calculate the iron (the main corrosion product) concentration at the boundary through the following equation [2]

$$c_w = \text{Min}(10^{6.01-4380/T}, co^{-4/3}10^{11.35-(12844/T)}), \tag{20}$$

where c_w is the surface concentration in ppm, c_O is the oxygen concentration in LBE and T is the absolute temperature in Kelvin.

The following parameters are used in the analysis:

loop/pipe length $L = 29.92$ m,

hydraulic diameter $d = 0.0525$ m,

kinematic viscosity of LBE $\upsilon = 1.5 \times 10^{-7}$ m^{2}s^{-1} [2],

liquid LBE velocity $V = 0.5 \, \text{ms}^{-1}$,

oxygen concentration in LBE $co = 0.01\text{ppm}$,

diffusion coefficient of iron in LBE : $D_{\text{Fe}\to\text{Pb}-\text{Bi}} = 10^{-9} \text{ m}^2\text{s}^{-1}$ (estimated based on data from Ref.[4]).

The Blasius equation [5] is used to calculate the friction factor λ and the expression developed by Berger & Hsu [6] to estimate the mass transfer coefficient K. They are

$$\lambda = 0.046 Re^{-0.20} \ (Re= Vd/\upsilon) \text{ and } K_{B-H} = 0.0165\upsilon^{-0.530}D^{0.670}V^{0.860}d^{-0.140}.$$

Three sets of the corrosion rates for pipe (hypothetically open) and closed loop flows based on the temperature profile are shown in Figure 2 for $T_{\text{max}} = 550^{\text{O}}\text{C}$. The figure illustrates the difference between the pipe and loop flow, and the effects of global temperature profile on the distributions of the corrosion.

For the pipe flow, there is no precipitation, the maximal corrosion occurs at the beginning of maximal temperature, while the minimal corrosion is at the intermediate temperature and its position moves downstream as the temperature variation becomes small. A smaller temperature gradient leads to higher corrosion rates and smaller variations.

For the closed test loop flow, the mean corrosion rate is zero. The integrated corrosion must equal to the integrated precipitation over the entire loop. The highest corrosion occurs at the beginning of loop section with the highest temperature, while the maximal precipitation takes place shortly after the temperature in the flow direction begins to decrease, and the location moves down stream as the temperature gradient decreases. Another difference between the pipe flow and loop flow is that a smaller temperature gradient leads to a smaller corrosion at the highest temperature section for the loop flow. The variation in the corrosion/precipitation rate becomes more significant as the temperature gradient increases. However, after the gradient exceeds a certain level,

the corrosion/precipitation rate changes very little with any further increase of temperature gradient.

To illustrate the effects of the maximal temperature, as well as the temperature gradient, on the corrosion rate at the test section. The surface plot of the mean corrosion rate in the hot test section as functions of the temperature gradient and the maximal temperature is shown in Figure 3. The corrosion rate increases with the temperature gradient and the change slows after the gradient exceeds 100ºC, and nearly saturates after reaching 200ºC. For the same gradient, the corrosion increases drastically with the maximal temperature. For accelerated corrosion testing, it is desirable to increase the testing temperature and set the temperature difference closer to 200 ºC.

It is demonstrated that the corrosion / precipitation distribution in a closed loop depends both on the global boundary concentration gradient and the local boundary concentration. To illustrate the intermediate temperature effects, Four corrosion / precipitation rates under different intermediate temperature for T_{Max}=550°C and T_{Max}-T_{Min}=200°C are shown in Figure 4. The intermediate temperature has strong influence on corrosion/precipitation rates and distributions through changing the temperature and surface concentration gradients. With the increasing intermediate temperature, the corrosion rate in the maximal temperature section is reduced, while in the first intermediate temperature section (in the forward flow direction), the corrosion rate is increased, and in the second intermediate temperature section, the location for the highest precipitation moves downstream. For the test samples located in the maximal temperature section in the test loop, it is desirable to reduce the intermediate temperature to reduce the test time.

This new understanding of the dependence of corrosion/precipitation rates on the global temperature distribution is very useful for helping to design and operate non-isothermal closed loop systems. We plan to verify the key aspects in future experiments. This dependence implies that the corrosion test results obtained from one flow loop can not be directly applied to another loop with a different temperature profile. It also suggests that it is possible to design flow systems to minimize corrosion and precipitation, or change the locations of maximal precipitation for enhanced system lifetime performance.

4. Discussions

By solving the governing mass transport equation in the boundary layer with the assumptions that the convective transport dominates in the longitudinal flow direction and the mass diffusion dominates in the transverse direction, we derive a corrosion model for isothermal and non-isothermal flow system. The present study corrects a minor error and extends the previous work [2] to more general cases. It also explains why using the average corrosion model would consistently overestimate the corrosion rate in closed loops [1].

Two configurations are considered in the present study: a closed loop flow and an open pipe flow. The mean corrosion/precipitation rate for a closed loop flow is zero, which means that it is the temperature gradient sustaining the corrosion process and precipitation is important. Corrosion in an open pipe flow is higher than that in the loop flow and there is no precipitation in the pipe flow.

To quantify the scaling dependence of the corrosion rate on hydrodynamic and transport parameters, the corrosion rate is rewritten in the following form:

$$q = \beta f(\xi) + K(c_0 - c_0{}^b). \qquad (21)$$

The function $f(\xi)$ depends only on the boundary condition. The parameter β, which may be called the mass transfer coefficient for the loop corrosion rate, is defined by

$$\beta = \frac{1}{\Gamma(1/3)Ai(0)}(\frac{2\pi D^2\gamma}{3L})^{1/3} = 0.3825\upsilon^{-0.27}D^{0.667}V^{0.60}d^{-0.067}L^{-0.333}. \qquad (22)$$

The equation above indicates that the kinetic corrosion / precipitation rate is proportional to $V^{0.60}$, $d^{-0.067}$ and $L^{-0.333}$. Accordingly the local corrosion rate increases with the flow velocity, and decreases with the loop/pipe length for the same temperature difference, but depends little on the pipe diameter.

The mass transfer coefficient is usually expressed in a dimensionless form by the Sherwood number:

$$Sh = \frac{Kd}{D}.$$

An analytical solution of Sh has been developed in Ref [5] for high Sc and constant boundary concentration. The solution is:

$$Sh = 0.0102Re^{0.90}Sc^{1/3} \qquad . \qquad (23)$$

If β is used to substitute the mass transfer coefficient K, we obtain

$$Sh_\beta = 0.3825Re^{0.60}Sc^{1/3}(d/L)^{1/3}. \qquad (24)$$

The above two equations indicate both forms of the Sherwood number have the same scaling with the Schmidt number. The dependence of Reynolds number for the average corrosion in a pipe flow is $Re^{0.90}$ and for the corrosion in a closed loop flow is $Re^{0.6}$.

The present study is confined to the constant hydraulic parameter cases, i.e. the hydraulic parameters do not change in the flow direction. In future studies, loops of multi-modules and multi branches shall be included. Another challenge in future work is the modeling the chemical reaction kinetics of the corrosion products and oxygen in the bulk flow, which is an important aspect in the active oxygen control technique.

Finally, the present model is only valid for the high Schmidt number flow, i.e. liquid metal flow, in which the mass diffusion layer is submerged under the hydraulic boundary layer. For small and intermediate Schmidt numbers, more sophisticated models are necessary to analyze the corrosion / precipitation phenomena.

4. Conclusions

The analysis of this corrosion model reveals three important attributes. First, the corrosion rate depends not only on the local temperature and flow conditions, but also on the global temperature profile. Second, in the non-isothermal closed loop flow, the local corrosion rate scales as $Re^{0.60}$ and $Sc^{0.333}$, and for an open pipe flow with constant boundary concentration, the corrosion rate scales as $Re^{0.90}$ and $Sc^{0.333}$. Third, for a closed loop flow, the average corrosion rate is zero in steady state and the local corrosion rate is smaller than that for pipe flow at the same condition.

For our LBE test loop, we find the highest corrosion rate at the beginning of the hot test section and the highest precipitation rate shortly after the hot test section. After the temperature gradient exceeds a certain level, the corrosion distribution changes little with further increase of the gradient. The highest and the intermediate temperatures have significant effects on the corrosion magnitude at the test section. For accelerated corrosion test, it is necessary to increase the highest temperature while reducing the

intermediate temperature. If possible the temperature gradient should be set close to 200°C.

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Figure captions

Fig.1 Temperature profile of the LBE test loop (MTL)

Fig 2 Corrosion rate under three conditions

Fig.3 The mean corrosion rate at the test section of the LBE loop as a function of the

temperature gradient and the maximal temperature.

Fig.4 Corrosion rate of the LBE loop for different intermediate temperatures.
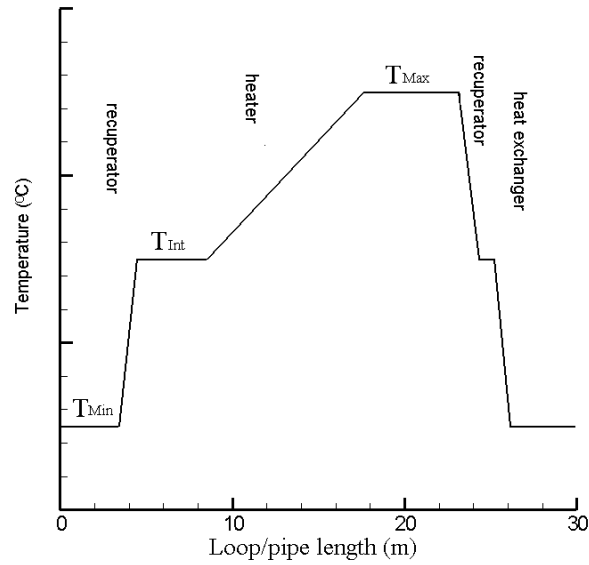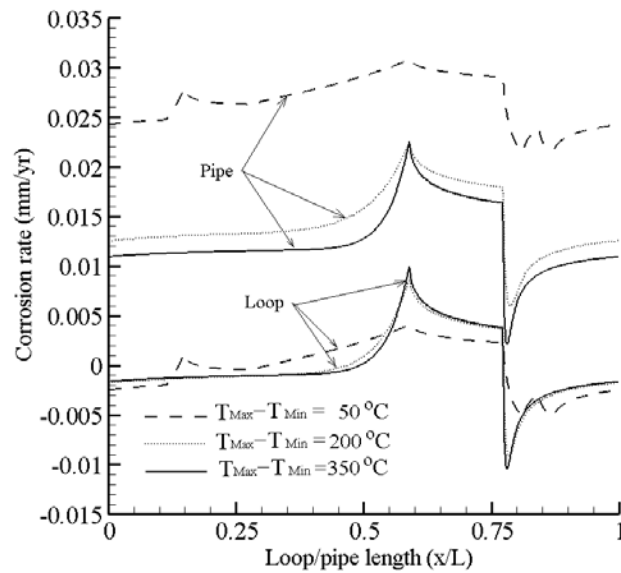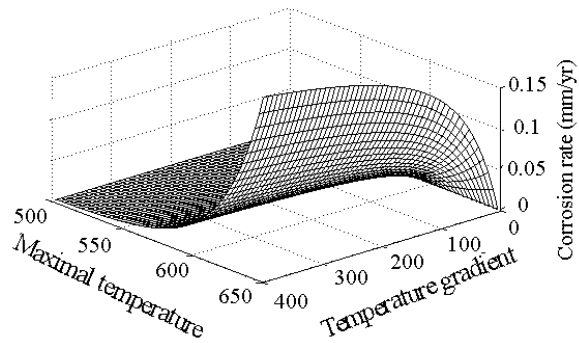
Fig.1 Temperature profile of the LBE test loop (MTL)

T_{Max}: the maximal temperature; T_{Min}: the minimal temperature; T_{Int}: the intermediate temperature.

Fig 2 Corrosion rate under three conditions

Fig.3 The mean corrosion rate at the test section of the LBE loop as a function of the

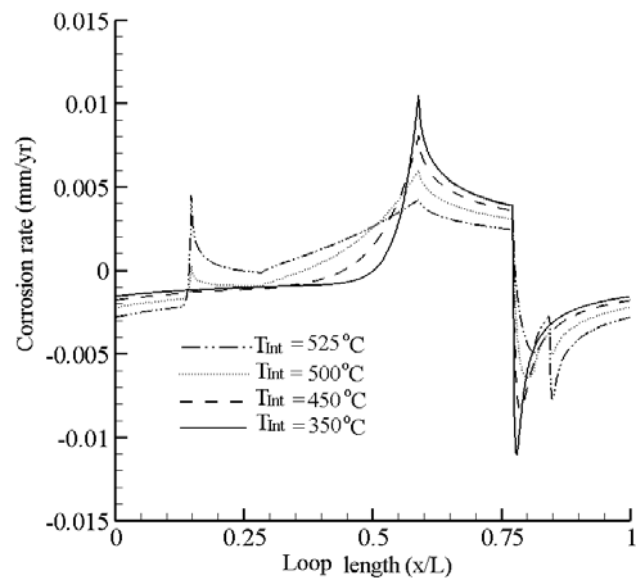temperature gradient and the maximal temperature.

Fig.4 Corrosion rate of the LBE loop for different intermediate temperatures.